

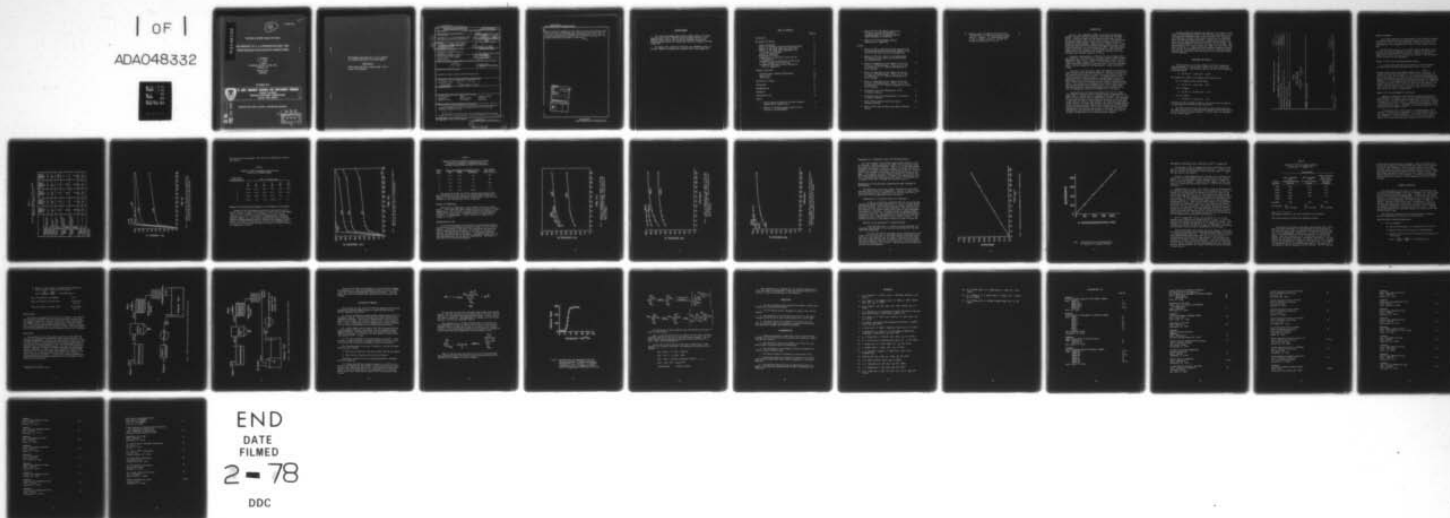
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THE REMOVAL OF 2, 4, 6-TRINITROTOLUENE (TNT)
FROM AQUEOUS SOLUTION WITH SURFACTANTS

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MILTON ROTH
ARRADCOM

OCTOBER 1977



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<p>2,4,6-Trinitrotoluene (TNT) has contaminated the wastewater emanating from plants engaged in not only the manufacture but also the loading, assembling and packing of TNT.</p> <p>It has been found that certain surfactants containing amino groups reacted rapidly with TNT in aqueous solution. The reaction product was a dark brown</p>		

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material which was insoluble in water. When the initial concentration of TNT was in the range of 120-140 ppm, after reacting with surfactant the TNT concentration in the filtrate was found to be at trace levels. Thus, this reaction was developed for the purification of wastewater containing TNT. The reaction mechanisms of the process is discussed.

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10 Relative rates of formation of TNT with the concentrations of 4-dodecyldiethylene triamine and 3,3' - diamino - N - methyldipropylamine at 25°C in aqueous solutions. Initial concentration of TNT was $2.5 \times 10^{-4}M$

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INTRODUCTION

The U.S. Army, ARRADCOM (Armament Research and Development Command) develops munitions processes and products for the Armed Forces. Production under full mobilization would make the Army the fourth largest industry in the United States. Large production requirements coupled with a broad variety of products result in various pollution problems. Among the most serious of these is the wastewater emanating from the plants manufacturing loading, assembling and packing 2,4,6-trinitrotoluene (α -TNT). These wastewaters contain mostly TNT, along with lesser amounts of other nitro compounds such as dinitrotoluene and isomers of TNT which are toxic, hazardous and frequently discolor the water.

Extensive investigations on treatment of the wastewater have been conducted. The processes so far investigated include bacterial degradation (Ref 1 and 2), carbon-adsorption (Ref 3 and 4), and adsorption on organic resins (Ref 5). At the present time, only the carbon adsorption technique is being utilized. A new less expensive process for the treatment of TNT wastewater is being continuously sought.

Initially it was intended to apply foam separation techniques to remove dissolved TNT from aqueous solution. Foam may be used to remove substances dissolved in a liquid by several processes known collectively as foam separation (Ref 6). The common feature of all these techniques is that separation is brought about by virtue of differences in the surface activity of the dispersed substances. These substances may be naturally surface active or rendered surface active. The surface active components are adsorbed and collected at the interface between gas and liquid phases. Air or other gases bubbling through the liquid generate gas-liquid interfaces and result in foaming which allows the interfaces to be collected.

Foam separations have been investigated for years to remove trace amount of metallic ions and certain organic compounds such as phenol (Ref 7), enzymes (Ref 8), naphthalene derivatives (Ref 9), and alkyl benzene sulfates (Ref 10) from aqueous solution. Work conducted for the past few years at the Polytechnic Institute of New York under a grant from the Office of Water Research and Technology, Department of the Interior, has shown that metallic ions such as cadmium, mercury, nickel and copper could be removed almost quantitatively from aqueous solution using surfactants (Ref 11 and 13) which chelated selectively with metallic ions and were concentrated in the foam. The foam was skimmed from the liquid and the surfactant was regenerated and recycled by decomposition of the surfactant-metal complex.

The foam separation technique was applied to the removal of dissolved TNT from aqueous solution. The surfactant initially used was 4-dodecyldiethylenetriamine and the TNT was effectively removed by this technique. However, under certain conditions, the surfactant formed an insoluble complex with TNT in aqueous solution and therefore, could be separated by filtration rather than by foaming. The initial concentrations of TNT was in the range of 100-150 ppm. The concentration of TNT in the filtrate was found to be less than 1 ppm. Since filtration is a simpler and more economical separation process than foaming, the investigations on the removal of TNT from aqueous solution with surfactants were redirected to use filtration instead of foam separation.

PROCEDURES AND RESULTS

The dark brown tar (reaction product of TNT and 4-dodecyldiethylenetriamine, 1:3 molar ratio, respectively) was isolated and dried under vacuum. The elemental analysis of the solid yielded the following results:

C: 58.74%; H: 6.64% and N: 20.29%.

The theoretical values of the complex were calculated as:

For 1:1 complex of TNT and the amine

C: 55.42%; H: 8.43% and N: 16.9%

For 1:2 complex

C: 61.30%; H: 10.30% and N: 16.5%

For 2:1 complex

C: 49.70%; H: 6.49% and N: 17.4%

According to these elemental analyses, the brown solid obtained was a mixed composition of TNT and the surfactant.

The brown solid was dried and found to burn without explosion. The impact sensitivity of the solid was examined at Picatinny Arsenal and it was found to be non-explosive. The test result is attached to this report (page 3).

PICATINNY ARSENAL, DOVER, NEW JERSEY 07801		SAMPLE NO.
REPORT FROM THE PROPELLANTS RESEARCH BRANCH		DATE
KIND OF SAMPLE	Explosive Composition	8 March 1976
RECEIVED FROM	Mod. & Sp. Tech. Div., MTD, Mr. M. Roth	REPORT NO.
REFERENCE OF X. O.	5462-19-003	76-PR-G-P-16
REPRESENTING	1 Sample of TNT Complex	DATE RECEIVED
		26 February 1976

RESULTS

Impact Sensitivity
2 Kg P.A. Impact Test

Height, Inches	Chg. wt., gms.
40+	0.007

PROCEDURE: Technical Report 3278, Rev. 1, except that the submitted sample was ground and tested without performing the granulation specified.

WORK BY: L. Jehl
SARPA Form 1243 Feb 74

SUBMITTED: N. Liszt, Chief, Instr. Anal. Rsch. Sect. APPROVED: F. J. Masuelli, Chief, Props Rsch Br.

General Procedures

2,4,6-Trinitrotoluene was obtained from Fisher Scientific Company. To simulate pink water, the saturated TNT aqueous solution was irradiated by UV light. The pink colored TNT solution was used in this investigation. The concentration of TNT was in the range of 120-150 ppm.

The pink TNT solutions (1-3 l) containing various amounts of surfactants were mixed by magnetic stirring. Samples (50-150 ml) were periodically taken and the solutions were filtered through filter paper with a filter aid such as celite or diatomite. The TNT content of the filtrate was then determined.

Removal of TNT Using 4-Dodecyldiethylenetriamine

An investigation was made on the removal of TNT from aqueous solution using 4-dodecyldiethylenetriamine ($\text{H}_2\text{N}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{NH}_2$,

$\text{C}_{12}\text{H}_{25}$

obtained from Eastman Kodak Company) under various conditions. A typical procedure was as follows: solutions (1 l) containing 1.29, 2.58, 3.87, 5.16, and 6.45 mole ratio of 4-dodecyldiethylenetriamine to TNT were prepared. The solutions were stirred at room temperature. Samples (60 ml) were periodically taken and the results are summarized in Figure 1. It was observed that the higher the ratio of concentrations of surfactant to TNT, the faster the rate of TNT removal. For example when the ratio was 6.45, only 15% of the original TNT was left in solution after 2 hours stirring and only 0.5% and 0.1% TNT left after 4 and 6 hours, respectively.

Removal of TNT Using Commercial Surfactants

Commercial surfactants containing amine groups were obtained from General Mills Chemicals Inc. and the Industrial Chemicals Division of Armak. The typical physical properties of the fatty diamine surfactants are listed in Table 1. Among these surfactants, N-tallow-1,3-diaminopropane ($\text{N}-\text{C}-\text{C}-\text{C}-\text{N}-\text{tallow}$) was the least expensive (55-59 cents per pound at Armak). Therefore, attention was directed to this surfactant for the removal of TNT.

A typical procedure using N-tallow-1,3-diaminopropane, was as follows: solutions (1 l) containing 1, 2, 3, and 6 molar ratios of the surfactant to TNT were prepared. The solutions were stirred at room temperature. After intervals of 2, 4, 6, 8, 10, 24, and 48 hours, 60 ml of each solution was filtered and the TNT content in

Table 1
Typical physical properties of fatty diamines
(General Mills Chemicals Inc.)

	N-Octyl-1, 3-propylene diamine (Diam 11)	N-Octyl-1, 3-propylene diamine (Diam 11C)	N-Tall Oil Fatty-1, 3-propylene diamine (Diam 15)	Distilled N-octyl-1, 3-propylene diamine (Diam 21D)	N-Tallow-1, 3-propylene diamine (Diam 26)
Melting Point, °C. (AOCS Official Method Cc 1-25)	30	32	29	25	47
Pour Point, °C. (ASTM D97-57)	21	20	16	0	30
Specific Gravity, 25°C./25°C. (ASTM D70-52)	0.85	0.85	0.85	0.84	0.85
Viscosity, centipoises (Brookfield) 30°C 60°C	18 11	24 7	18 9	11 6	semisolid 8
Surface Tension (1) dynes/cm, 25°C. (DuNuoy Interfacial Tensiometer) Saturated Solution 0.1% 0.01%	— 28 27	— — —	— 29 15	— 29 30	48 — —
Interfacial Tension (2) dynes/cm, 25°C. (DuNuoy Interfacial Tensiometer) 1.0% 0.1% 0.01%	4 7.0 23	— — —	4 5 17	2 15 40	3 5 33
Free Point, °C. (ASTM D92-57)	223	215	221	165	215
Flash Point, °C. (ASTM D92-57)	196	196	188	140	190

(1) Aqueous solution
(2) Nujol solution

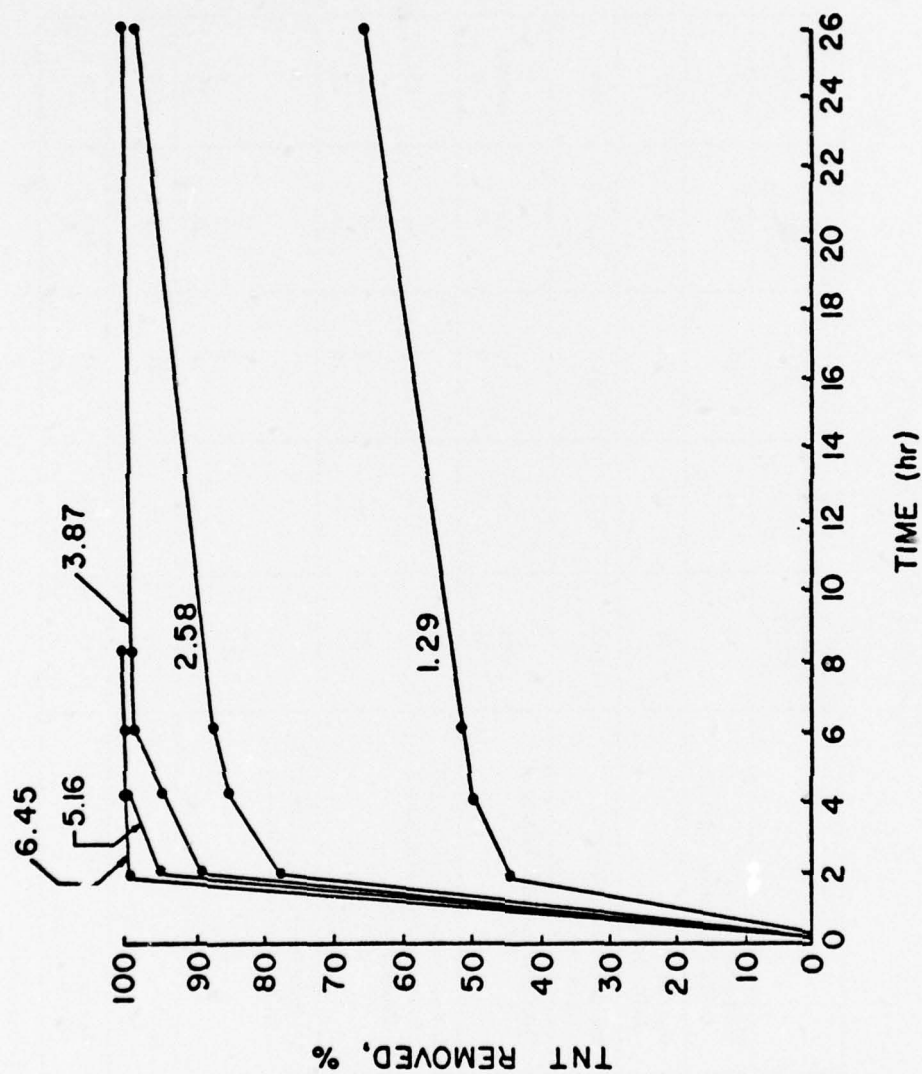


Fig 1 Removal of TNT vs time with various concentrations of 4-dodecyltriethylenetriamine (the numbers on the curves are the molar ratio of surfactant/TNT)

each filtrate was determined. The results are summarized in Table 2 and Figure 2.

Table 2
Removal of TNT from aqueous solution using
N-tallow-1,3-diaminopropane

Mole ratio (surfactant/TNT)	TNT in filtrate, ppm					
	0 hr	2 hr	4 hr	6 hr	28 hr	48 hr
1	65.0	44.3	41.0	38.7	33.6	28.2
2	65.0	25.4	22.6	21.2	15.8	10.5
3	65.0	15.8	12.7	11.1	5.1	0
6	65.0	2.3	1.0	<0.05	0	0

Removal of TNT Using Amine Compounds in the Presence of Surfactants

Removal of TNT from aqueous solutions was also carried out by adding a mixture of amine and surfactant to pink water at room temperature. Several solutions (1 l) containing 5.5×10^{-4} M of TNT (125 ppm), 6.0×10^{-4} M of N-methyl-1,3-diaminopropane (Jefferson Chemical Company, Inc.) and various concentrations of a surfactant, hexadecyltrimethylammonium bromide, (Eastman Kodak Company) were prepared. The removal of TNT from the solutions was determined after 25 hours with the procedure described in Section II-A and the results are summarized in Table 3.

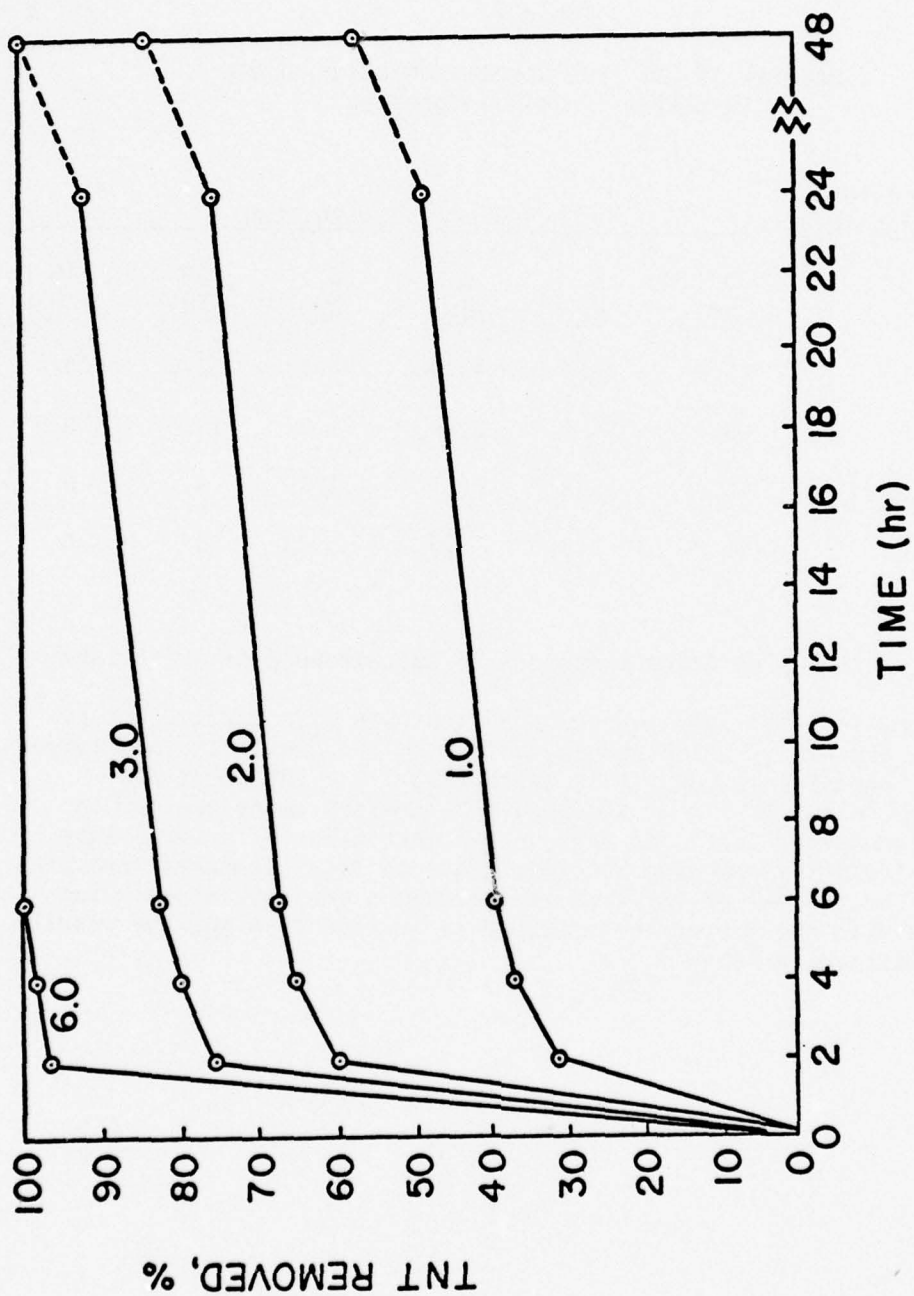


Fig 2 Removal of TNT with N-tallow-1,3-diaminopropane (the numbers on the curves are the molar ratio of surfactant/TNT)

Table 3

Removal of TNT from aqueous solutions by (an amine)
a mixture of N-methyl-1,3-diaminopropane and
hexadecyltrimethylammonium bromide (a surfactant)

Sample No.	Conc in the original solution, 10^{-4} M			TNT removed after 25 hr, %
	TNT	Amine	Surfactant	
1	5.5	6.0	2.0	84
2	5.5	6.0	4.0	97
3	5.5	6.0	5.0	100
4	5.5	6.0	6.0	98
5	5.5	6.0	>10.0	~ 0

The results show that the TNT was removed quantitatively when the concentrations of TNT, amine and surfactant were almost equal. However, it was found that the degree of the removal of TNT was very sensitive to the concentration of the surfactant.

Effects of Temperature

The effects of temperature on the removal of TNT were investigated. It was found that faster removal of TNT was obtained at higher temperatures. Thus, the TNT in aqueous solution was quantitatively removed at 80°C using only two equivalent moles of the surfactant, N-tallow-1,3-diaminopropane. Typical results are summarized in Figures 3, 4, and 5.

Determination of TNT

2,4,6-Trinitrotoluene water solution has an absorption maximum at 230 nm with an extinction coefficient of about 2.2×10^4 (Ref 14). However, in treatment of TNT waste, this absorption band cannot be used to determine the concentration of TNT since the solution also contains some impurities or additives. A colorimetric procedure that was specific for TNT in wastewater, developed by Mudri (Ref 15), was found applicable for the present investigation. The method is described in the following paragraphs.

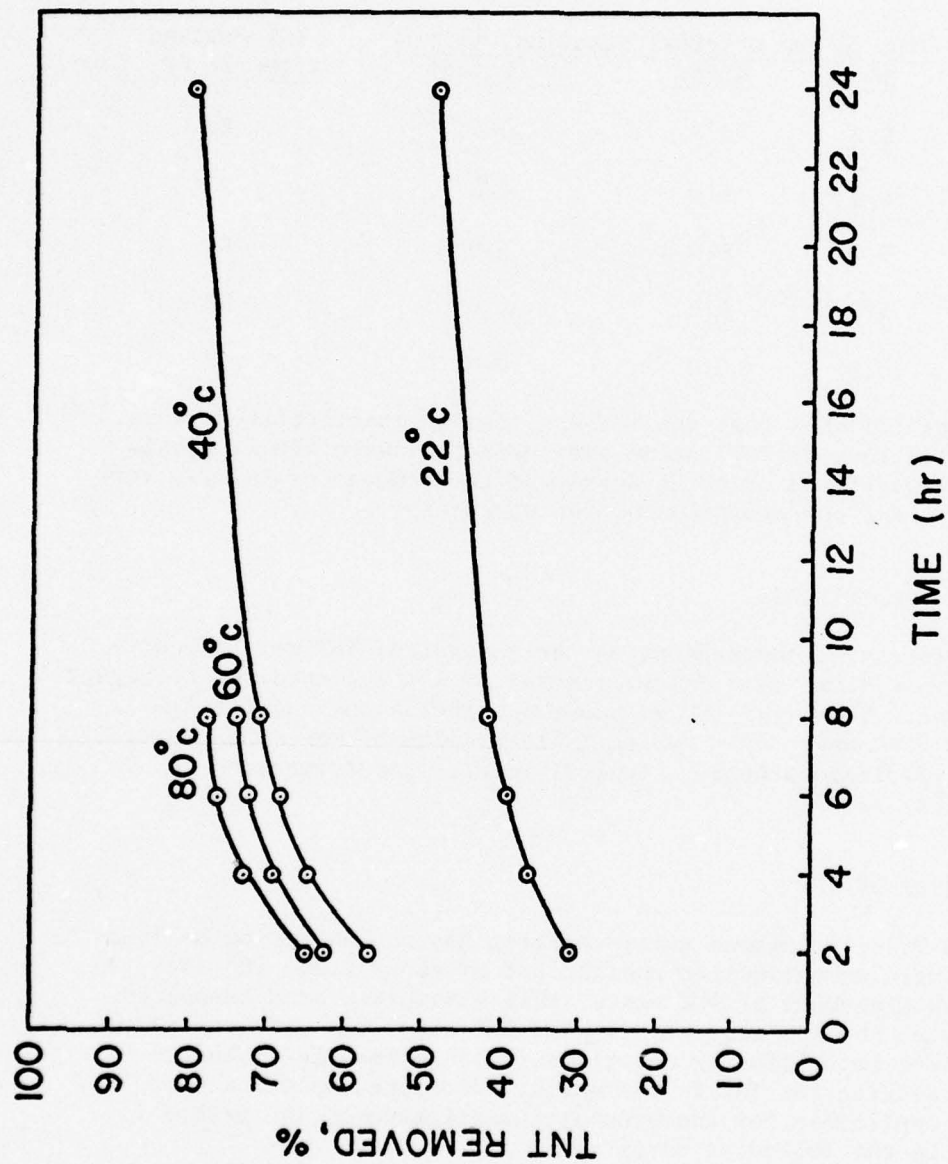


Fig 3 Effect of temperature on the removal of TNT with N-tallow-1,3-diaminopropane. Molar ratio of TNT to surfactant is 1:1. Initial concentration of TNT is 140 ppm

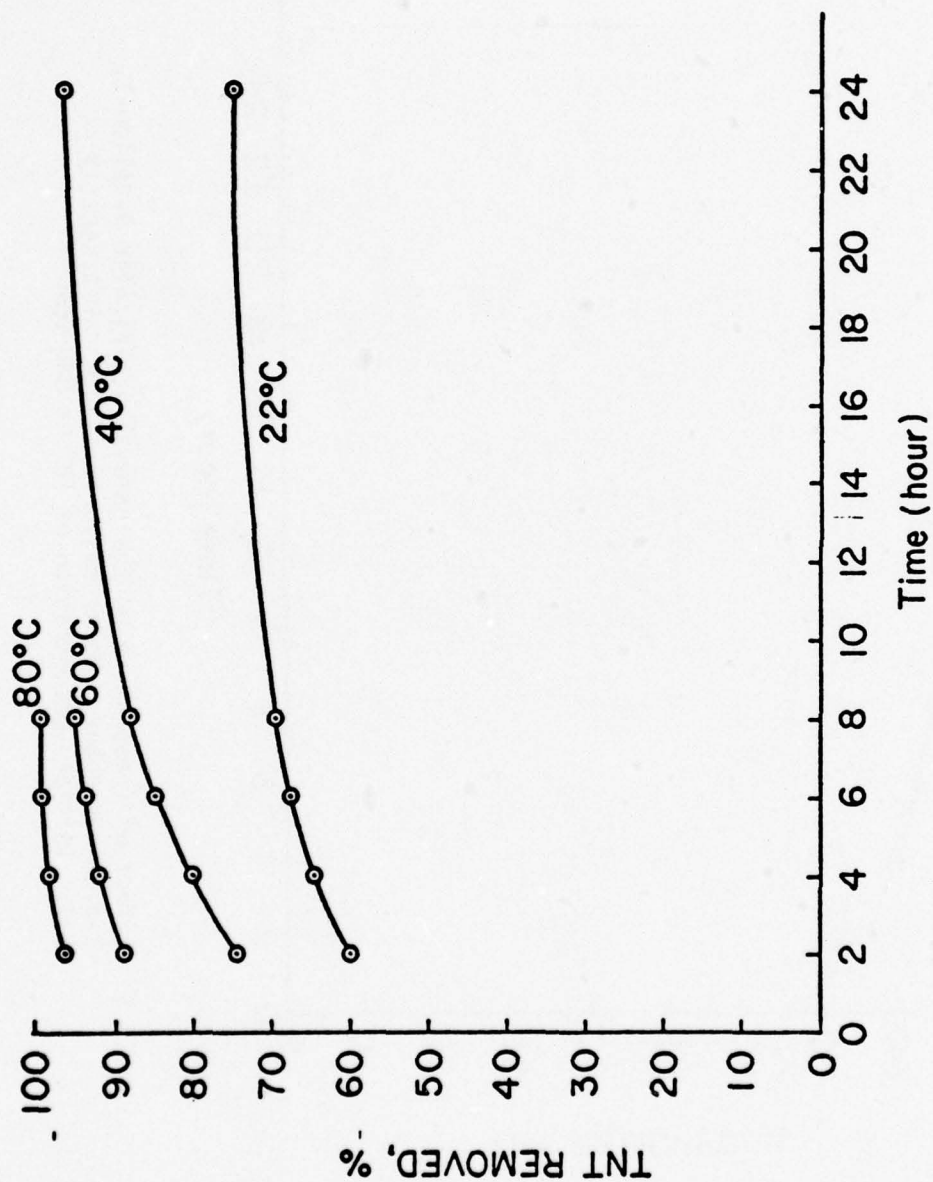


Fig 4 Effect of temperature on the removal of TNT with N-tallow-1,3-diaminopropane. Molar ratio of TNT to surfactant is 1:2. Initial concentration of TNT is 140 ppm

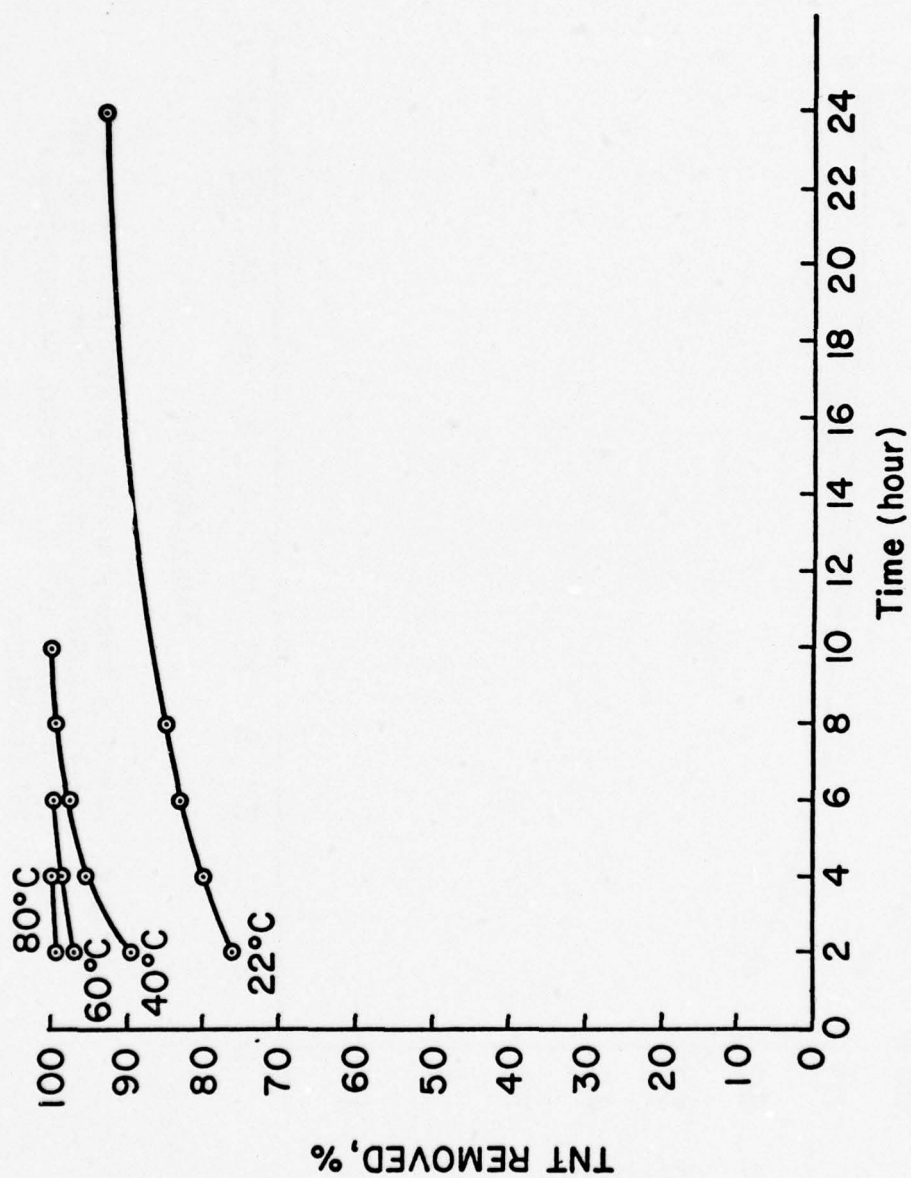


Fig 5 Effect of temperature on the removal of TNT with N-tallow-1, 3-diaminopropane. Molar ratio of TNT to surfactant is 1:3. Initial concentration of TNT is 140 ppm

Preparation of a Calibration Curve for TNT Determination

To a 25 ml sample of the freshly prepared TNT solution, 2.5 ml of 10% Na_2SO_3 (freshly prepared) was added. The solution was mixed and allowed to stand for 5 minutes. Then 0.5 ml of 10% NaOH reagent was added, with mixing, allowed to stand for 10 minutes and the absorbance was recorded, using water as reference, at 500 nm. The maximum color was reached at 10 minutes after the addition of both reagents. The intensity of color remained constant for 5 minutes and then faded gradually thereafter. Therefore, the readings were taken 10 to 15 minutes after both reagents were added. The absorbance vs the amount of TNT was a straight line relation (Fig 6).

Determination of the Surfactant Concentration after Treatment of TNT Solution

The surfactants used in the present investigation were linear alkylated amines which are biodegradable. However, in order to find the concentration of the surfactant in the filtrate after TNT removal, the following experiments were carried out.

Preparation of a Calibration Curve for Surfactant

To 100 cc of solutions containing 200, 150, 100, and 50 ppm 4-dodecyldiethylenetriamine respectively, 2.5 ml of 1% CuSO_4 aqueous solution was added. The solutions were well shaken and kept for one hour until the blue color was fully developed. Then, the spectrum was recorded in the visible region using a Cary-14 spectrophotometer with water as a reference. In order to obtain an optimum reading, 10 cm cells were used. The wavelength at 615 nm offered maximum absorbance of color. The absorbance vs the concentration of the surfactant was found to follow Beer's law, as shown in Figure 7. This relation holds even if the solution contains as much as 5 ppm TNT.

Analysis of the Surfactant in Treated TNT Waste

After the pink water was treated with the surfactant, the surfactant concentration in the filtrate was determined by the procedure described above.

From the TNT removal experiments using surfactant/TNT ratio 2.58, 3.87, 5.10, and 6.45, it was found that the surfactant concentrations in the filtrates were 10-20 ppm. These results show that the excess surfactant was also filtered out, and this was confirmed when only 18 ppm was found in the filtrate after a solution containing 200 ppm surfactant was filtered. Similar results were found with N-tallow-1,3-diaminopropane.

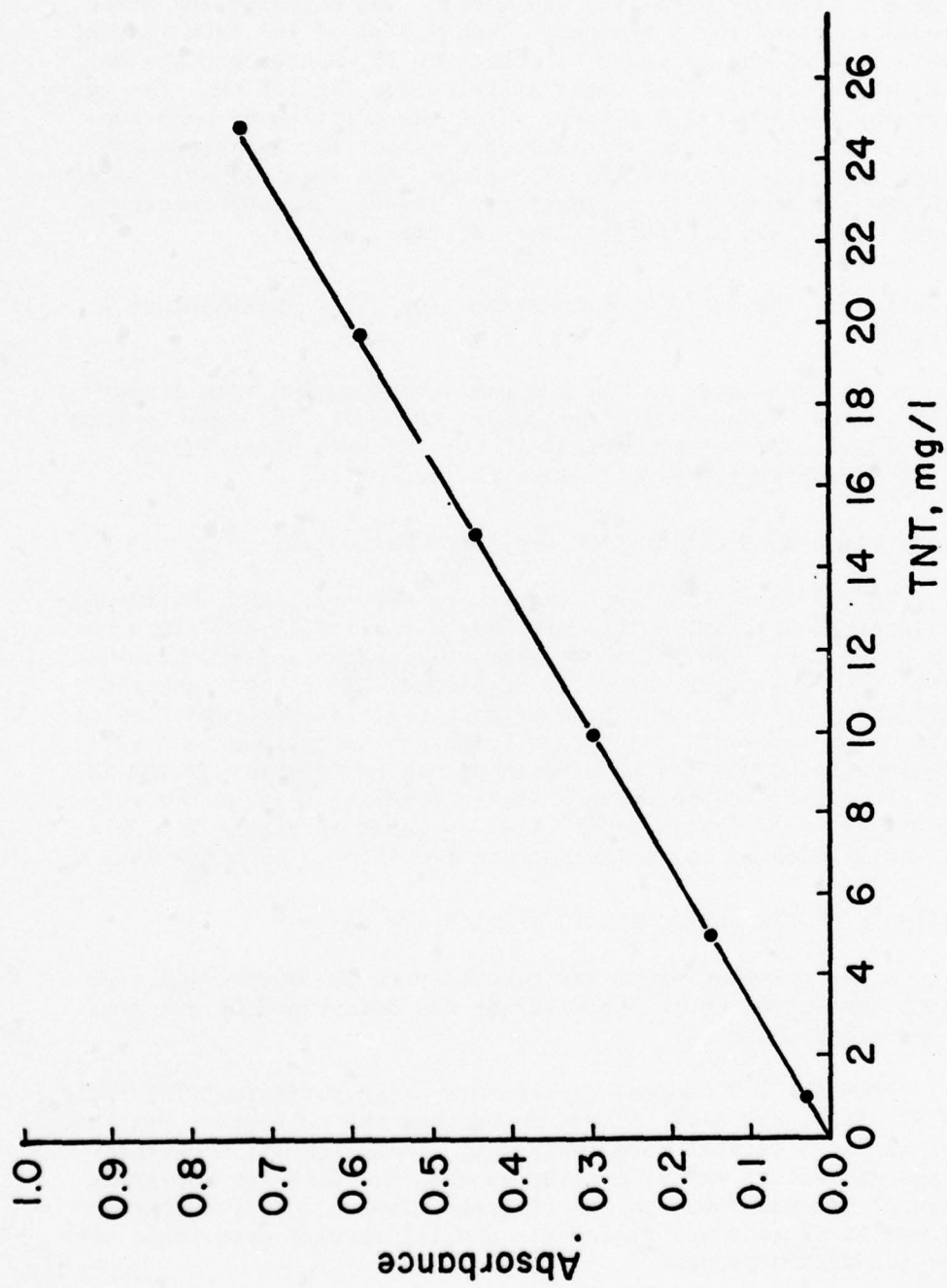


Fig 6 Calibration curve for determination of TNT in aqueous solution

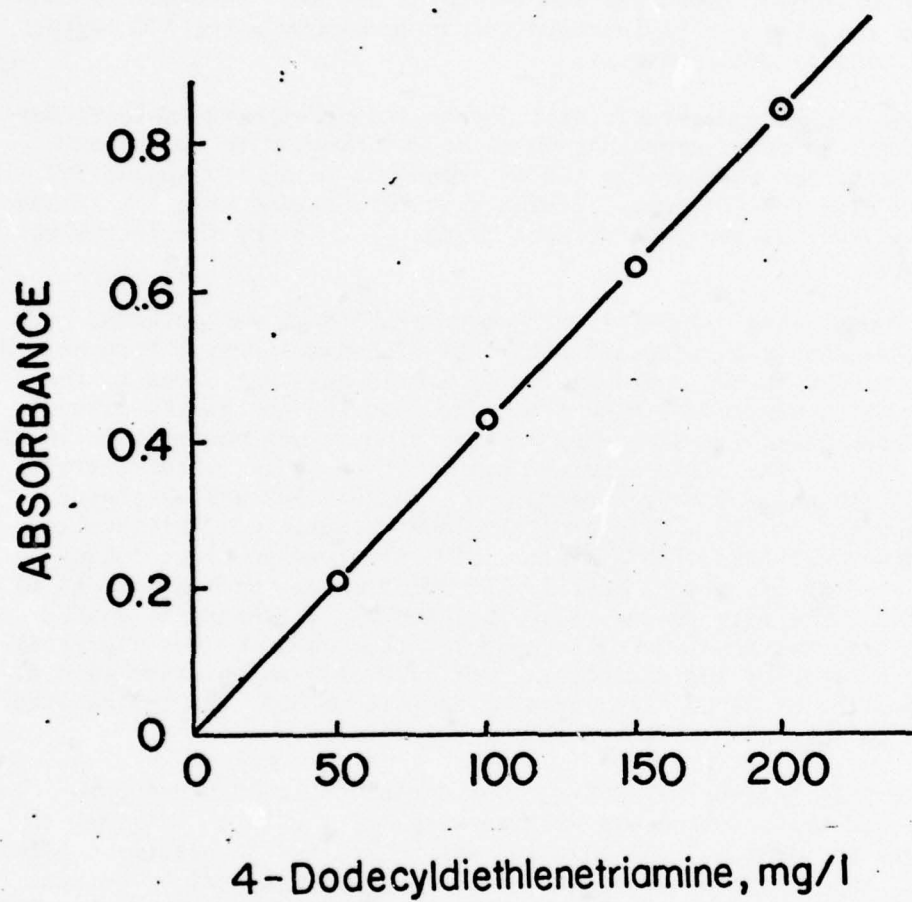


Fig 7 Calibration curve for determination of surfactant in aqueous solutions

TNT Removal Experiments Using a Radioactive TNT (^{14}C Tagged TNT)

The analysis of TNT in aqueous solution was performed using the Cary 14 instrument measuring absorbance at 525 nm. In order to confirm the results, the radioactive tracer technique using ^{14}C tagged TNT was used for the analysis.

Since it is conceivable that the treatment with surfactants may convert TNT to other compounds which do not respond to the colorimetric test, the radioactive tracer technique using ^{14}C tagged TNT was also used for analysis. Radioactive TNT, tagged with ^{14}C in the ring, was synthesized from toluene (ring -1- C-14) by the following procedure:

Toluene (ring -1- C-14), 0.25 m Curie, 5.8 mg was obtained from New England Nuclear and mixed with 1 ml of nonradioactive toluene. A mixture of 6 ml H_2SO_4 and 4 ml fuming nitric acid was added to the toluene which was cooled with ice. The solution was gently warmed over a free flame for 3 minutes and the product was poured into 20 ml of ice water. The solid obtained was purified by recrystallization from 90% ethanol. 2,4-Dinitrotoluene (ring 1-C-14) was obtained; melting point 70.5°C . Then 5 ml of oleum solution of dinitrotoluene was further nitrated with a mixture of 1 ml oleum and 1 ml fuming nitric acid at 115° for 2 hours. The solution was poured into 10 ml ice water. The pale yellow solid isolated was filtered and washed several times with water. The crude TNT thus obtained was recrystallized from ethanol and radioactive TNT, 700 mg, was obtained with a melting point of 80°C . The infrared spectra of both the synthesized and the commercially obtained TNT were identical.

The C-14 tagged TNT, 500 mg, was dissolved in 10 ml of pure acetone and the solution was diluted with 3.5 l water. In order to eliminate the acetone, the solution was boiled for 30 minutes. After cooling, the solution was made up to 4 l by adding water. The concentration of the TNT (125 ppm by weight) was determined by measuring the absorbance (Cary 14) and was calculated to be 123.3 ppm.

Various experiments were carried out on the removal of TNT from the radioactive solution using 4-dodecyldiethylenetriamine and N-coco-1, 3-diaminopropane (ArmaK Co.). The TNT solutions (1000 ml) containing 4-dodecyldiethylenetriamine (mole ratio 1:2) and N-coco-1,3-diaminopropane (mole ratio 1:3) were prepared. The solutions were stirred for 40 hours at ambient temperature. The brown precipitate produced was filtered off and the filtrate (2 ml) was dissolved into 15 ml of Aquasol counting solution (New England Nuclear). The radioactivity was determined by the liquid scintillation counter (Nuclear-Chicago Unilux).

Table 4
Removal of TNT from aqueous solution
containing C-14 tagged TNT^{a,b}

Initial solution	Counts/Minute		
	After treatment with 4-dodecyldiethylene triamine	After treatment with N-coco-1,3-diamino propane	After extraction with CH ₂ Cl ₂ without amino- surfactant treatment
83828	3245	3779	678
84028	3375	3733	646
83344	3233	3830	715
83922	3420	3727	672
83892	3327		
Avg 83803	3320	3767	680
TNT 125 ppm	TNT calc 4.88 ppm	TNT calc 5.55 ppm	TNT calc 0.94 ppm

^aThe aqueous solution (5 ml) was diluted with 18 ml Aquasol.

^bThe blank solution of Aquasol was counted as 50/min.

The results of the tracer experiment indicated that after treatment with amine surfactant, the concentrations of TNT remaining in the filtrates were 4.9 ppm for dodecyldiethylenetriamine and 5.6 ppm for N-coco-diaminopropane, respectively. In order to check these results, the concentrations of TNT were determined by the absorption method. They were calculated to be 0.50 ppm and 0.51 ppm for the dodecyl and coco-amine surfactants treatments, respectively. The discrepancy of the analytical results was accounted for by the contamination of dinitrotoluene (C-14 tagged) in the initial TNT (C-14 tagged); the absorption (UV) of 2,4-dinitrotoluene shows at 250 nm which is distinguished from the absorption of TNT (230 nm). The TNT solutions,

filtered after amino-surfactant treatment, showed the absorption at 250 nm and the amounts of dinitrotoluene were found to be as much as 4-5 ppm for both solutions. Since the amino-surfactant treatment could not remove dinitrotoluene from aqueous solution, the initially contaminated dinitrotoluene remained in the filtered solution. Therefore, these experiments showed that the TNT in aqueous solution was removed quantitatively by the treatment. The result also confirmed that the TNT did not convert to other compounds which are dissolved in water.

ECONOMIC EVALUATION

The major expense in the process is that of the surfactant and N-tallow-1,3-diaminopropane is one of the cheapest that could be used. This surfactant is available from Armak. Therefore, the TNT removal process uses N-tallow-1,3-diaminopropane. It was found that the efficiency of the removal of TNT depended on the initial molar ratio of surfactant to TNT, temperature, and reaction time. As shown in Figure 2, when the initial molar ratio of surfactant to TNT is increased, the removal time is decreased. The theoretical amount of the surfactant required is one mole for two moles of TNT (assuming the mechanism described in the Discussion in this report). However, the optimum amount of the surfactant required is between two to four moles per mole of TNT.

The Recurring Differential Cost Calculation (the differences between alternatives are itemized) are listed below:

Recurring Costs (Production/Operation)

1. Cost of surfactant

- a) Based on 600,000 gal w.w. (150 ppm TNT) 750 lbs TNT
- b) Based on \$0.57/lb of N-tallow-1,3-diaminopropane
- c) Based on 3 molar ratio of surfactant/TNT and 48 hrs reaction time:

$$\$0.57 \times \frac{750}{227.11} \times \frac{242 \times 3}{600} = \$2.28/1000 \text{ gal w.w.}$$

- d) Based on 2 molar ratio of surfactant/TNT (Removal of TNT, 0.50 ppm to 1 ppm at 40°C for 48 hrs)

$$\$0.57 \times \frac{750}{227.11} \times \frac{242 \times 3}{600} = \$1.52/1000 \text{ gal w.w.}$$

2. Cost of landfill of the complex	\$0.02
Total cost based on 3 molar ratio	\$2.30/1000 gal w.w.
Total cost based on 2 molar ratio	\$1.54/1000 gal w.w.

Capital Costs

The capital investment of this process is minimal. The existent TNT wastewater treatment plant can be used with small modification. For example, Figure 8 is a sketch of the bomb or shell washing plant at ARRADCOM using activated carbon adsorption for wastewater treatment. The layout of the proposed modified plant is shown in Figure 9. The additional equipment for this process include a surfactant feeder and a stirring mixer but the carbon adsorption columns are eliminated.

Other Costs

The operation cost of this process requires a small amount of electricity, operating and maintenance labor, repair material, and instrument maintenance. There are too many counteracting factors and too many unknowns to permit quantitative estimates of operating costs. This process can also be applied to the TNT contaminated wastewater effluent from a TNT manufacturing plant. The cost effectiveness of chemical treatment has been well demonstrated against corresponding capital expansion¹. In nearly all cases, chemical treatment comes out ahead. One of the more compelling arguments for chemical treatment is that it can be used on an interim basis while necessary capital expansion is arranged. In some cases, capital expansion may be delayed or possibly even eliminated by the use of chemical treatment with existing plants.

¹C&E News, p 36, Dec 13, 1976.

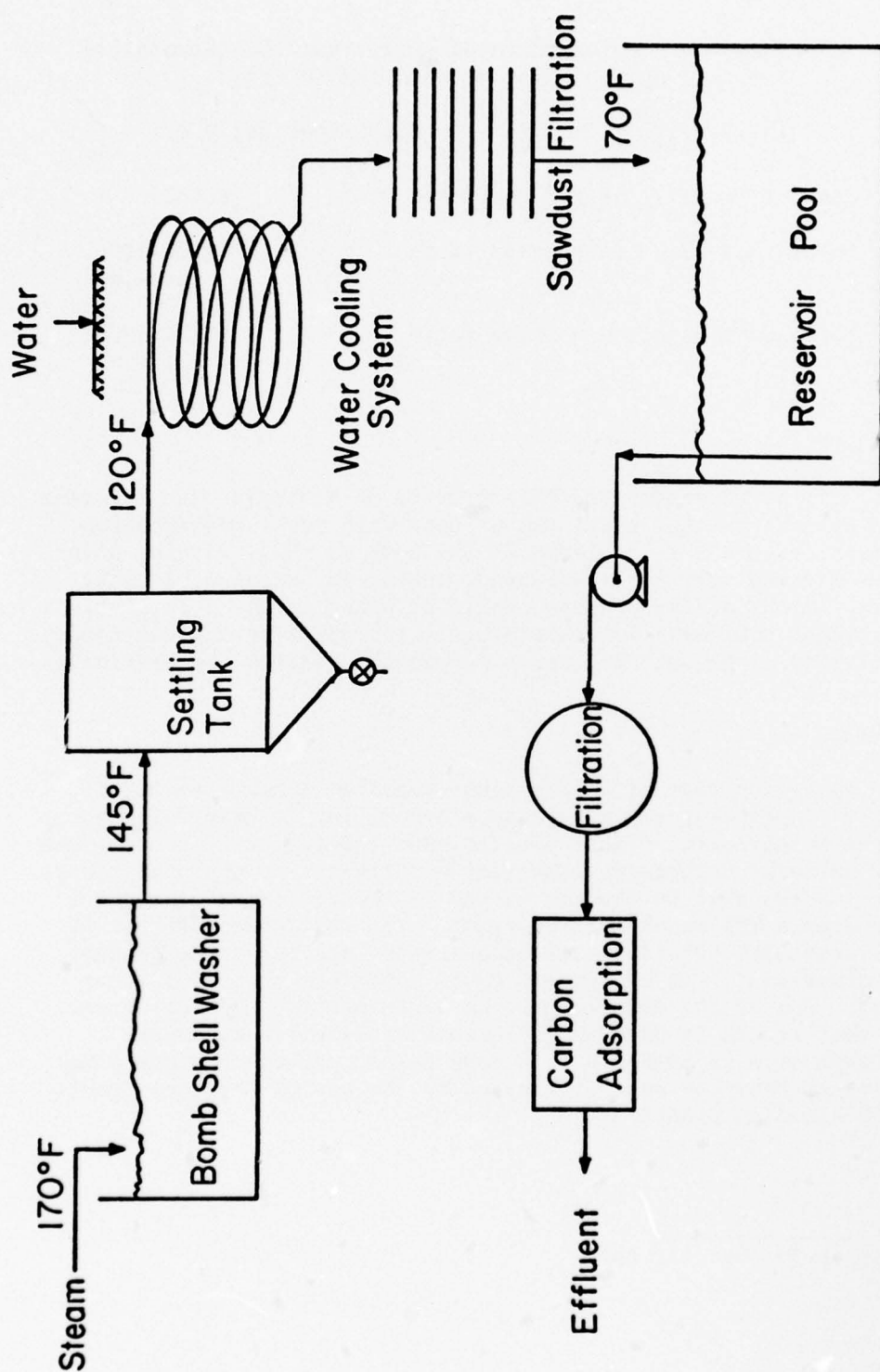


Fig 8 Bomb or shell wash-out plant with carbon adsorption process

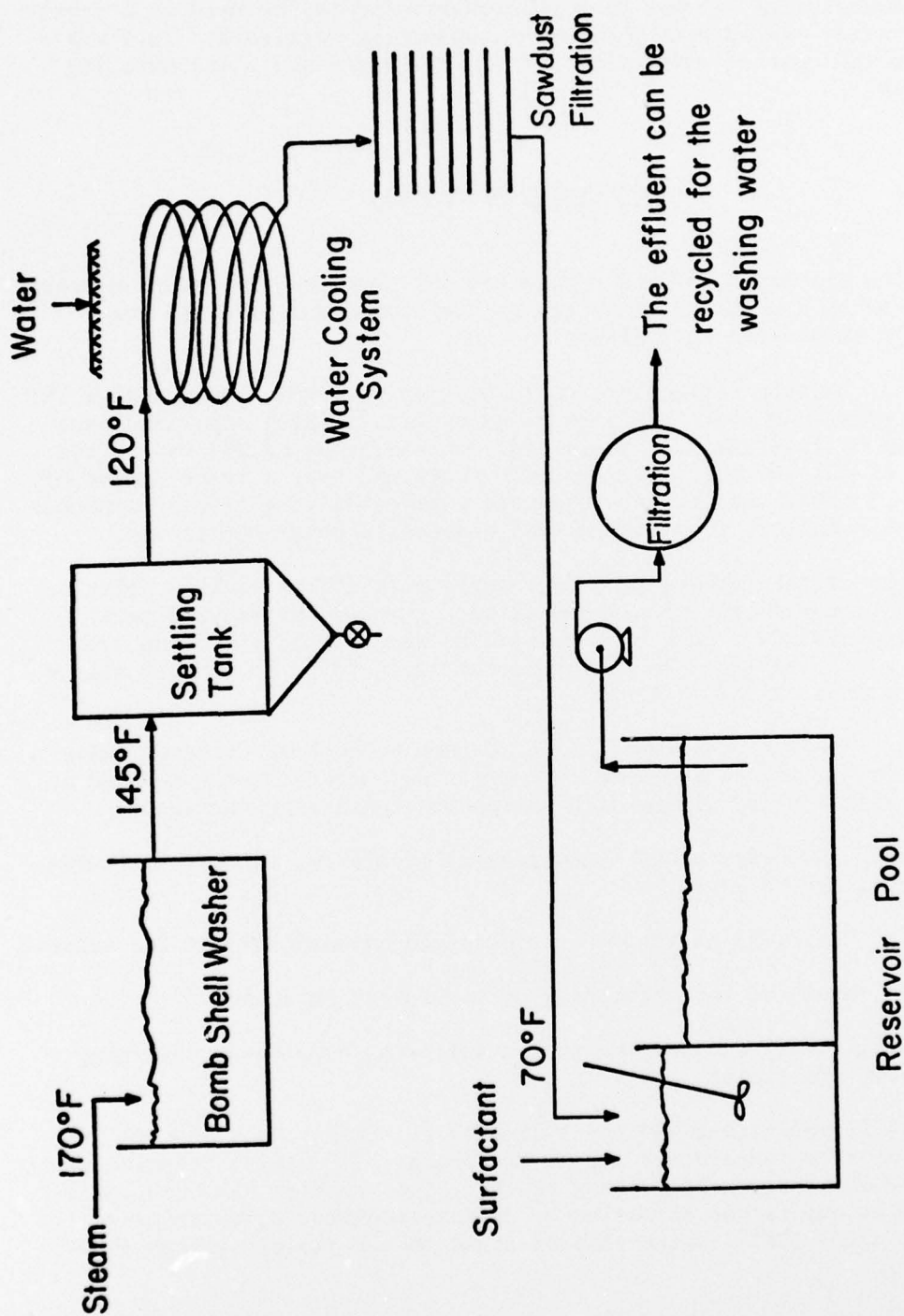


Fig 9 Bomb or shell wash-out plant with added surfactant process

Since the dark brown solid complex is a nitro-enriched compound and nonexplosive, it may be biodegradable and may be used as a fertilizer after mixing with phosphorus containing nutrients. This may reduce the cost of surfactant and eliminate the solid incinerating problem.

DISCUSSION OF PROCESS

The processes for the removal of TNT from aqueous solution using surfactants containing amino groups are simple and safe and are briefly summarized as follows:

a) Certain surfactants containing amino groups reacted with TNT in aqueous solution. The dark brown particles which separated were removed by filtration. The initial concentration of TNT was in the range of 120-150 ppm. The filtrate contained only a trace amount of TNT (< 1 ppm). Surfactants used are commercially available compounds such as N-tallow-propyldiamine and N-dodecyldiethylenetriamine.

b) Certain amines reacted readily with TNT in aqueous solution in the presence of cationic surfactants such as hexadecyltrimethylammonium bromide. Dark brown particles were precipitated and separated by filtration. The filtrate was again found to contain only a trace amount of TNT (< 1 ppm).

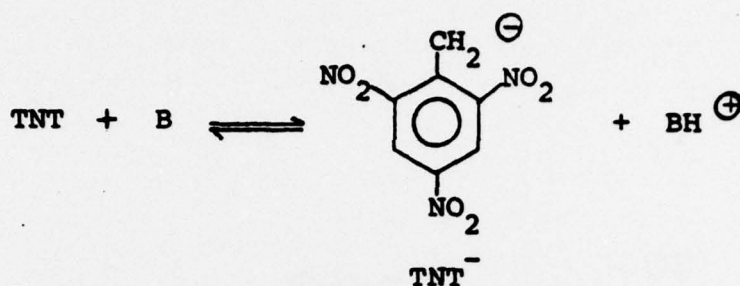
c) The solid isolated can be burned without any hazard. Alternatively, it may be feasible to compost product or it may be used as a fertilizer after mixing with phosphorus containing nutrients.

This invention opens a new area of chemistry, and the following questions may be asked:

- 1) What kind of reactions took place between TNT and the amines?
- 2) What are the structures of the solids obtained?

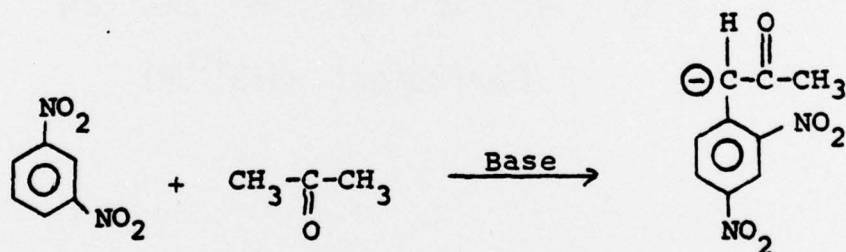
Preliminary studies led to the following hypotheses regarding the above questions:

It is known that TNT has a limited solubility ($\sim 5 \times 10^{-4}$ M) in water at room temperature and produces a highly colored solution when reacted with strong bases (Ref 16-20). The reaction has been interpreted as due to the formation of an intermediate, 2,4,6-trinitrobenzyl anion (TNT^-) which absorbs light in the visible region (500-525 nm).



The reaction rate was very slow when simple amines were reacted. However, the rate was found to be increased (50 to 150-fold) with the addition of a surfactant containing an amine group. Typical results are shown in Figure 10. The enhancement is thought to be due to the micellar effect of the surfactant (Ref 21).

The production of an intense coloration when a solution of m-dinitrobenzene in acetone is treated with alkali was first noted by Janovsky and Erb in 1886 (Ref 16) and is now known as the Janovsky reaction. The colored product obtained in the reaction is recognized as the anion from the corresponding 2,4-dinitrobenzyl ketone.



When 2,4-dinitro and 2,4,6-dinitro and 2,4,6-trinitrotoluenes were reacted with base, the anions initially produced reacted with unreacted nitro compounds to yield a complex.

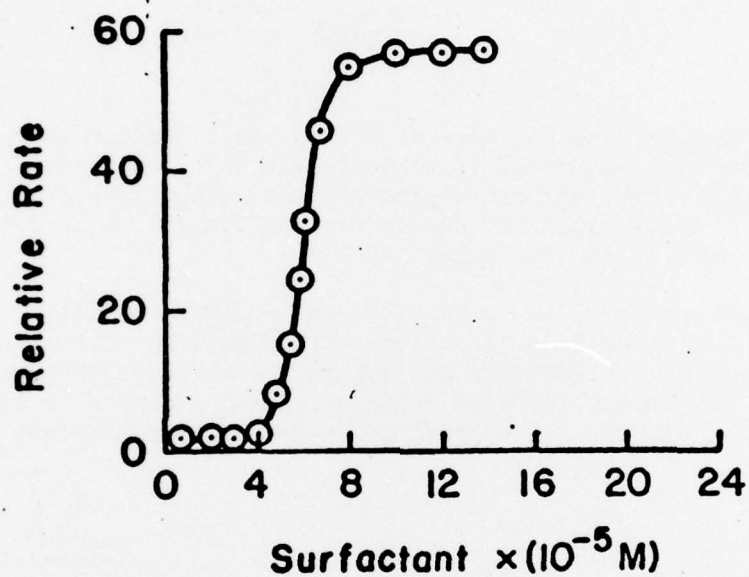
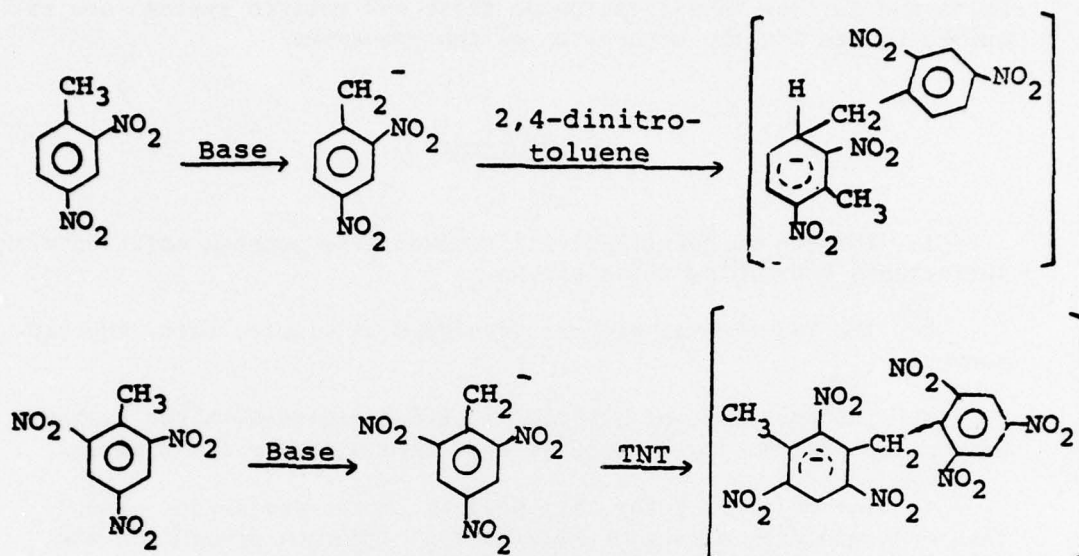


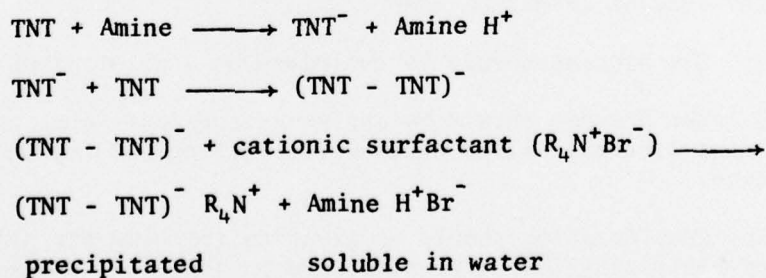
Fig 10 Relative rates of formation of TNT with the concentrations of 4-dodecyldiethylene triamine and 3,3' - diamino - N - methyl-di-propylamine at 25°C in aqueous solutions. Initial concentration of TNT was $2.5 \times 10^{-4} \text{ M}$



The structures of these complexes were postulated on the basis of their visible spectra.

Thus, in the reaction of TNT with amine, the TNT^- anion initially produced could react with TNT to form the Janovsky complex. The complex reacted with the protonated surfactant and precipitated as a salt: $(\text{TNT} - \text{TNT})^-(\text{surfactant H})^+$.

In the case of the reaction of TNT with a simple amine in the presence of a cationic surfactant, the hypothetical reactions are as follows:



These hypotheses were suggested by very limited experimental results and further investigation on these and related systems are required to clarify the mechanisms of the processes.

CONCLUSIONS

1. TNT can be quantitatively removed from aqueous solution with surfactants containing amino groups.
2. The TNT removal process developed is simple, safe, and economical.
3. The equipment of existing wash-out plants with the carbon adsorption process can be used so that capital costs are minimal.
4. The major cost for this process is the surfactant used. This cost would be offset by elimination of carbon adsorption and more definitive economic data should be obtained.

RECOMMENDATIONS

1. Further discussion be sought with various surfactant manufacturers as to the availability of suitable and inexpensive surfactants for this process.
2. The utilization of the solid product as a fertilizer and other biomass resources should be investigated.
3. The structure(s) of the complex should be determined and toxicity studies should be made.
4. The process should be evaluated on a pilot plant scale.
5. The process should be evaluated for wastewater containing other dissolved explosives such as RDX, nitroglycerin, and nitroguanidine.
6. Consideration should be given to applying the process to lagoons containing TNT wastewaters and to soils contaminated with explosives.

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